

## Total cross sections for electron scattering on chloromethanes: Formulation of the additivity rule

Grzegorz P. Karwasz, Roberto S. Brusa, Andrea Piazza, and Antonio Zecca\*

*Dipartimento di Fisica, Istituto Nazionale per la Fisica della Materia, Università di Trento, 38050 Povo (Trento), Italy*

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Total cross sections for electron scattering on  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$  have been measured by an absolute method in the (75–4000)-eV energy range. The overall experimental error is below 5%. A formulation of the additivity rule is proposed. The molecular cross sections are approximated by a Born-like two-parameter formula. We show that the low-energy parameter is correlated to the molecular polarizability. We show also that the high-energy parameter for a given molecule can be expressed as the sum of the high-energy parameters of the constituent atoms. The model has been successfully verified for two groups of halomethanes: the  $\text{CH}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  series and the  $\text{CF}_4$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ , and  $\text{CCl}_4$  series. The model has been successfully extended to molecules containing Si and S atoms, such as  $\text{H}_2\text{S}$ ,  $\text{SF}_6$ ,  $\text{SiH}_4$ , and  $\text{SiF}_4$ . [S1050-2947(99)10102-1]

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### I. INTRODUCTION

Chlorine substituted methanes play an important role in atmospheric chemistry [1]; their time in the Earth's troposphere is several tens of years. Free Cl radicals formed by ultraviolet-induced dissociation act as catalysts in the chain of reactions leading to the destruction of the stratospheric ozone [2]. In particular, chloromethane ( $\text{CH}_3\text{Cl}$ ), used in refrigerators and organic chemistry, is the most abundant halocarbon present in the atmosphere.  $\text{CH}_3\text{Cl}$  is also the most frequently studied halocarbon in electron-scattering experiments.

The early measurement of total cross sections (TCSs) for electron scattering on  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  were performed by Holst and Holtmark [3] at energies between 1 and 25 eV. The Maryland group [4,5], using a trochoidal spectrometer, covered the range up to 12 eV for all the gases of the  $\text{CH}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  series. The total cross section for  $\text{CH}_3\text{Cl}$  was also studied by Krzysztofowicz and Szmytkowski [6] at (0.5–200)-eV collision energies in a linear-transmission experiment. The  $\text{CF}_4$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ , and  $\text{CCl}_4$  series and  $\text{CH}_4$  were studied in a time-of-flight experiment up to 50 eV by Jones [7,8].

Elastic and vibrational-excitation differential cross sections at 0.5–9.5 eV on  $\text{CH}_3\text{Cl}$  were studied by Shi *et al.* [9,10] and electron transmission spectra at 5–10 eV were studied by Spence [11]. Intermolecular interference effects in elastic scattering of 1 keV electrons on oriented methyl halides were studied by Meier *et al.* [12] and Bowering *et al.* [13].

Absolute photoabsorption and photoionization of  $\text{CH}_3\text{Cl}$  were measured by a forward electron-scattering method in the (6–350)-eV and (11–80)-eV ranges, respectively [14]. Electron attachment to chloromethanes was studied in numerous experiments by both electron-beam [5,15–18] and

swarm [19–22] techniques. Absolute ionization cross sections on  $\text{CH}_3\text{X}$  compounds (with  $X=\text{H}$ ,  $\text{F}$ ,  $\text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$ ) up to 200 eV have been recently measured by Vallance *et al.* [23] and the effects of the molecular orientation on ionization steric ratios in  $\text{CH}_3\text{Cl}$  and  $\text{CHCl}_3$  were measured by Aitken *et al.* [24]. The present total-cross-section measurements on  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$  complete our previous TCS data for  $\text{CH}_4$  [25] and the  $\text{CF}_4$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ , and  $\text{CCl}_4$  series [26].

### II. EXPERIMENT

Only minor adjustments and calibration checks were performed on the apparatus after our measurements for the  $\text{CF}_4$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ , and  $\text{CCl}_4$  series [26]. Briefly, a transmission method with a transverse magnetic field (a Ramsauer configuration) was used. The scattering chamber was divided in two parts to improve the angular resolution; the first part, containing the target gas, was 140.2 mm long. The beam attenuation was measured for a number of pressures in the scattering chambers at a given energy. The target gas pressure was maintained within the  $10^{-1}$ -Pa range, depending on the cross section being measured, in order to prevent the effects of multiple scattering. Both the collector current  $I_c$  and the current  $I_s$  of scattered electrons reaching the gas chamber walls were monitored; this allows one to reduce systematic errors caused by electron emission instabilities. The total cross section  $\sigma$  is evaluated from the formula

$$\frac{I_{ci}}{I_{ci}+I_{si}} = \frac{I_{cj}}{I_{cj}+I_{sj}} \exp[-\sigma l(N_i - N_j)], \quad (1)$$

where indices  $i$  and  $j$  refer to two gas pressure values  $p_i$  and  $p_j$  with  $p=NkT$ . ( $l$  stands for the gas cell length,  $T$  for the gas temperature, and  $k$  for Boltzmann's constant.)

The target gas pressure was measured by a Baratron capacitance meter and the two currents  $I_c$  and  $I_s$  by a single electrometer; the Baratron head traced the gas cell temperature within 0.1 °C in order to avoid the thermal transpiration

\*Electronic address: zecca@science.unitn.it

TABLE I. Experimental total cross sections for electron scattering on chloromethanes in units of  $10^{-20}$  m<sup>2</sup>. Statistical percentage errors (one standard deviation of the mean value) are given in parentheses.

Energy (eV)	CH <sub>3</sub> Cl	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>
75	21.7 (5.8)	28.9 (0.5)	35.2 (1.3)
80	20.7 (1.6)	27.5 (1.3)	34.2 (2.7)
90	19.3 (1.6)	26.1 (1.3)	33.0 (2.7)
100	18.3 (1.4)	25.1 (1.7)	31.9 (1.4)
110	17.1 (1.5)	24.0 (1.4)	30.8 (0.7)
125	16.3 (1.3)	22.1 (3.0)	28.8 (0.7)
150	14.4 (2.1)	20.0 (1.1)	26.6 (1.0)
175	13.3 (2.4)	18.5 (1.1)	24.1 (1.8)
200	12.3 (1.4)	17.3 (0.5)	22.7 (0.7)
225	11.7 (0.5)	16.8 (0.6)	20.9 (0.3)
250	11.0 (0.4)	15.7 (1.3)	19.9 (0.5)
275	10.3 (1.0)	14.7 (0.6)	18.9 (0.5)
300	9.76 (0.7)	14.3 (1.1)	18.3 (0.8)
350	8.80 (0.3)	12.6 (0.6)	16.6 (0.8)
400	7.92 (1.2)	11.6 (1.4)	15.5 (1.1)
450	7.28 (1.0)	10.6 (1.1)	14.0 (1.9)
500	6.72 (1.4)	9.90 (1.1)	13.3 (0.9)
600	6.00 (0.6)	8.81 (0.9)	11.5 (2.7)
700	5.19 (1.8)	7.82 (1.2)	10.2 (2.5)
800	4.62 (1.2)	7.36 (2.2)	9.49 (0.4)
900	4.22 (0.7)	6.51 (3.3)	8.69 (0.7)
1000	3.87 (0.7)	6.24 (2.5)	7.91 (1.2)
1100	3.67 (1.9)	5.70 (1.8)	7.33 (1.4)
1250	3.28 (0.5)	5.15 (3.2)	6.86 (0.9)
1500	2.73 (0.8)	4.34 (1.0)	5.87 (1.0)
1750	2.42 (0.9)	3.80 (1.5)	5.14 (1.0)
2000	2.19 (0.4)	3.40 (0.8)	4.75 (1.6)
2250	1.87 (2.3)	3.10 (1.1)	4.36 (1.3)
2500	1.71 (3.7)	2.83 (1.2)	3.84 (2.6)
2750	1.60 (1.7)	2.64 (3.6)	3.47 (2.8)
3000	1.48 (2.3)	2.49 (4.0)	3.14 (3.9)
3250	1.38 (3.1)	2.37 (4.2)	2.91 (2.8)
3480	1.28 (3.4)	2.19 (4.6)	2.89 (2.9)
4000	1.16 (3.7)	1.82 (0.5)	- -

uncertainty. The main contributions to the systematic error come from the Baratron calibration. The overall systematic error, evaluated as a quadratic sum of single contributions, is within 2.8%. This configuration does not include the angular resolution error, which depends on the particular target.

Several (at least four) runs were performed at each energy for five to seven pressure values. The statistical spread of data (one standard deviation of the mean value) is within 3%. Fewer runs were performed at (3000–4000)-eV energies in CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub>. At these energies, chlorine-containing ions and radicals formed in electron collisions cause sputtering and react chemically with the oxide-coated cathode. Therefore, a frequent cathode substitution was required. Consequently, the statistical uncertainty of the high-energy data for these two gases is higher; see Table I.

All absolute TCS measurements performed by the transmission method are affected by an angular resolution error related to the finite angular acceptance of the collector. The

error is due to the forward elastic and inelastic scattering. In the high-energy limit, where the Born approximation applies, the elastic differential cross section (DCS) at zero angle remains constant, while the integral cross section drops like  $E^{-1}$ . This causes the angular resolution error in the elastic channel to rise linearly with the collision energy.

The average angular acceptance of the present apparatus is 0.34 msr. We are not aware of measured or calculated DCSs in the zero-angle limit for chloromethanes. Bromberg [27] has performed measurements for CH<sub>2</sub>F<sub>2</sub> in the range 300–500 eV, showing that the elastic DCSs in the limit of small momentum transfer coincide at all collision energies. This indicates that the regime of Born validity is achieved for CH<sub>2</sub>F<sub>2</sub> at a few hundred eV. Comparing Bromberg's zero-angle DCS with the expected total cross section in CH<sub>2</sub>F<sub>2</sub> (see Sec. IV), we can estimate that the elastic scattering at 1000 eV contributes an angular resolution error less than 1% of the TCS.

In the inelastic channel, a limited ( $\Delta E/E \approx 1/16$ ) energy screening of the present apparatus eliminates the error for energies below, say, a few hundred eV. At higher energies the error in the inelastic channel can be bigger than in the elastic one because electrons involved in dipole-allowed electronic excitation and ionization collisions are forward peaked. Unfortunately, the lack of calculated or measured DCSs for the investigated molecules impedes any quantitative evaluation. On the other hand, further reducing the angular acceptance of our apparatus would lead to a lower electron current at the collector and a higher measurement uncertainty. Therefore, with the present choice of apertures [26], the upper energy limit of measurements has been established at 4000 eV, i.e., where the angular resolution error (in the elastic channel) is evaluated as approximately equal to the remaining systematic and statistical errors.

CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> liquids (Carlo Erba, Italy) stabilized with amylene were of 99.5% and 99% purity, respectively. CH<sub>3</sub>Cl gas of 99.5% purity was supplied by Praxair (Belgium).

### III. MEASUREMENT RESULTS

Our measured data for CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub> are presented in Fig. 1 and Table I. We can compare our TCS with the measurements of Krzysztofowicz and Szymtkowski [6] for CH<sub>3</sub>Cl. The agreement in the overlapping energy range 75–200 eV is rather poor, with 15% discrepancy on average. To exclude any possible error due to target contaminations a check measurement was performed at overlapping energies using the gas bottle from Gdansk [6]. The results of our check were in perfect agreement with those obtained with the previous bottle. Therefore, we are not able to determine the origin of this discrepancy. We note, however, that for other gases such as CH<sub>4</sub> [25], CF<sub>4</sub>, and CCl<sub>4</sub> [26,28] the agreement between the two laboratories was always within a few percent. Our previous measurements performed on the same apparatus, say, for CCl<sub>4</sub>, agree also with other TCS determinations [8,29].

In Fig. 1 our present data for CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub>, together with our previous CH<sub>4</sub> [25] and CCl<sub>4</sub> [26] results, are compared to the theory of Jiang *et al.* [30]. These authors applied a complex-optical-potential method in the

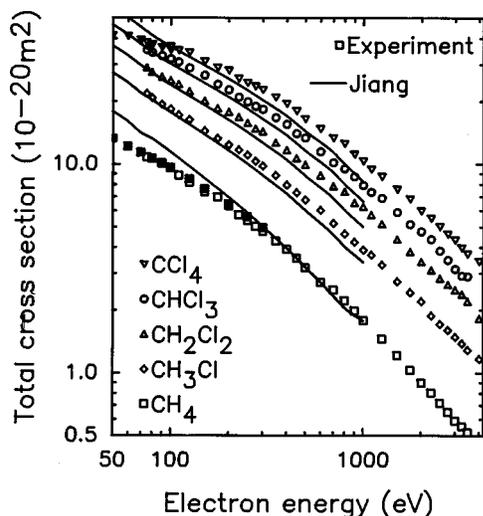


FIG. 1. Comparison between experimental data for chloromethanes (present data and [25,26]) and theoretical values of Jiang *et al.* [30]. For  $\text{CH}_4$  the low-energy data of Kanik *et al.* [31] are also shown (full squares); for  $\text{CCl}_4$  the data of Szmytkowski *et al.* [28] are shown only below 100 eV (full inverted triangles).

calculation of atomic total cross sections for H, C, F, Si, S, and Cl. They used Hartree-Fock atomic functions and atomic polarizabilities to derive the elastic cross sections. A semi-empirical absorption potential was used for the calculation of the inelastic cross sections. TCSs for different molecules (including  $\text{CH}_4$ ,  $\text{CCl}_4$ ,  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{SiH}_4$ , and  $\text{SF}_6$ ) were obtained by the simple arithmetic sum of these atomic contributions.

A set of atomic cross sections given by Jiang *et al.* [30] has been used by us to evaluate TCS values for the whole  $\text{CH}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  series. The values reported in Fig. 1 have been calculated using the simple additivity formulation of Jiang *et al.* The agreement between such a theory and experimental results is generally poor. The theoretical values for  $\text{CH}_4$  below 400 eV are higher than all the available measurements [25,31].

For other gases presented in Fig. 1 the theory agrees reasonably well with the present experiment only at 100 eV. The theory falls below the present data at higher energies (by more than 20% at 1000 eV for  $\text{CCl}_4$ ). Also, for  $\text{CH}_4$  the theory shows an energy dependence steeper than the experiment. Any correction of the present data for the angular resolution error would increase the discrepancy of this theory at high energies. We note also that the discrepancy cannot be accounted for by the size of the experimental error.

A comparison of the present measurements with the ionization cross sections confirms our earlier observation for  $\text{CF}_4$ ,  $\text{CCl}_3\text{F}$ , and  $\text{CCl}_4$  [26] on a much lower contribution to TCSs from the ionization in halides than in similar hydrides. According to the data of Vallance *et al.* [23], the ionization cross section at 100 eV amounts to 31% of the total cross section in  $\text{CH}_3\text{Cl}$ , about 33% in  $\text{CHCl}_3$ , and as much as 39% in  $\text{CH}_4$  (the last number is also in accordance with the most recent experiment of Tian and Vidal [32]).

#### IV. ADDITIVITY RULE FORMULATION

The hypothesis that integral cross sections for molecules can be obtained by an arithmetic sum of atomic contributions

(“additivity rule”) dates to Brüche [33]. It is now supported by the independent-atom model, applied successfully to elastic scattering on targets such as  $\text{O}_2$  [34] and  $\text{CF}_4$  [35] above, say, 400 eV. Recently it has become generally accepted that the additivity rule can provide a simple method for calculating molecular cross sections. Research is being done to give the correct formulation of the additivity rule and to establish the limits of validity [30,36]. In particular, it is believed that the rule can be applied above a certain energy only. However, the low-energy limit of validity remains to be established.

In the most recent applications of the additivity rule for the total cross section a different approach has been proposed [37]. The optical potential used at low energies was modified by including a molecular polarizability instead of the sum of atomic polarizability values. This allowed the extension of the validity of the additivity rule to lower energies; however, the calculated values at 50 eV still remain higher by 25–30% than the experiments for such targets as  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{NH}_3$  [37]. As already quoted, Jiang *et al.* [30] have used an additivity rule in its simplest form for energies from 10 eV to 1 keV. A modified additivity rule (with atomic weighted factors) has also been recently applied to molecular ionization cross sections [38]. In our previous studies [39,40] a two-parameter fit has been applied to approximate TCSs in the (100–4000)-eV energy range:

$$\sigma(E) = \frac{\sigma_z}{1 + \sigma_z E/b}, \quad (2)$$

where  $\sigma_z$  and  $b$  are two adjustable values for each target. In this range, Eq. (2) reproduces molecular TCSs within the experimental error bars. Equation (2) has been applied to many targets, for some of them such as  $\text{N}_2$ ,  $\text{CO}$  [40], and  $\text{SF}_6$  [41] down to the energy of a few tens of eV. This simple fit enables the parametrization of the TCS for different molecules in a large energy range and one to perform relative comparisons, reducing substantially the statistical spread of data. The theoretical basis for Eq. (2) comes from the Born approximation for scattering on a screened Coulomb potential (see [39]).

A more refined relation has been proposed in some of our previous papers [26,42]. For noble gases [42], an additional term was used in Eq. (2). In this work we limit our discussion to Eq. (2) strictly and we refer to  $\sigma_z$  as to a low-energy “saturation” value of the TCS and to  $b$  as a high-energy parameter.

The present semiempirical analysis of the fit parameters  $\sigma_z$  and  $b$  for molecules consists of two steps. First, we search for a correlation between the fit parameter  $\sigma_z$  and molecular properties of targets and then we explore a possible additivity rule for molecular TCSs.

Before discussing an alternative formulation of the additivity rule, we will show the results of a search for correlations between the  $\sigma_z$  parameter and macroscopic molecular properties of the targets. In the energy range below 200 eV, different semiempirical studies [43–45] indicated a possible relation between TCSs, at a chosen energy, and the molecular polarizability  $\alpha$ . Lampe, Franklin, and Field [46] indicated a linear dependence between the target polarizability and the ionization cross sections at 75 eV. Recently, Harland

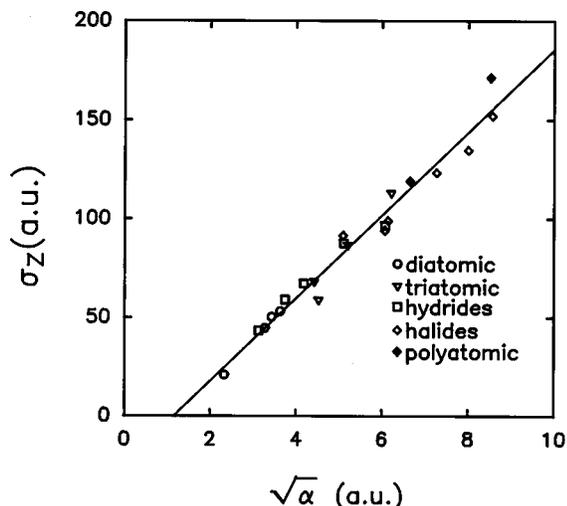


FIG. 2. Correlation between the molecular dipole polarizability and asymptotic “low-energy” cross-section parameter  $\sigma_z$  [Eq. (3)]. The values of  $\sigma_z$  are from our previous papers:  $N_2$  and  $CO$  [40];  $H_2$  and  $O_2$  [60];  $CO_2$ ,  $NO_2$ ,  $SO_2$ , and  $OCS$  [61];  $CH_4$ ,  $H_2O$ ,  $NH_3$ , and  $SiH_4$  [39];  $CF_4$ ,  $CF_3Cl$ ,  $CF_2Cl_2$ ,  $CFCl_3$ , and  $CCl_4$  [26];  $SiF_4$  [62];  $SF_6$  [41]; and  $C_6H_6$  [63]. (For the  $H_2S$  [39] [Eq. (2)] fit, taking account of the low-energy data of Szmytkowski and Maciąg [64] yields  $\sigma_z = 24.0 \times 10^{-20} \text{ m}^2$ .) The polarizability values are from [52]. The gases measured herein,  $CH_3Cl$ ,  $CH_2Cl_2$ , and  $CHCl_3$ , are not included in this figure.

and Vallance [47] indicated a similar dependence at the maximum of the ionization cross section for almost 30 molecular species. The above attempts are of limited interest as long as they involve a correlation to cross sections at a single energy. It is also known that the polarizability is related to atomic and molecular features such as the ionization potential [48], the strength of the van der Waals interaction [49], or the molecular volume [50].

In the present study we check a possible relation between the parameter  $\sigma_z$  in Eq. (2) and  $\alpha$ . In this way the correlation becomes independent of the choice of the particular energy at which the comparison is performed.

Classical models (see, e.g., [51]) for scattering of charged particles on a polarization potential suggest a linear proportionality dependence between the total cross sections and the square root of the polarizability. In Fig. 2 we present a plot of the parameter  $\sigma_z$  vs  $\sqrt{\alpha}$  for 20 molecular targets measured previously in our laboratory. Details of the fitting procedure used to derive  $\sigma_z$  were described in our previous papers [39,42].

For the sake of self-consistence all the polarizability values in Fig. 2 were taken from [52]. In the cases where more results were presented, the mean value was adopted. Note that the data of [52] are somewhat higher than reported by other compilations [53] and the results obtained from photo-absorption-like experiments in the optical and ultraviolet range [54,55]. In the majority of cases the quoted discrepancies disappear when the vibrational contribution to the molecular polarizability (see [56]) is added. This is, for example, the case of  $CF_4$ , for which the vibrational contribution amounts to 25% of the overall polarizability. As the vibrational excitation plays an important role in intermediate-energy electron scattering, we adopted the “to-

tal” polarizability from [52] rather than the purely electronic-excitation polarizability from other sources. As seen in Fig. 2, the  $\sigma_z$  parameter can be approximated well by the expression (in a.u.)

$$\sigma_z = 20(\sqrt{\alpha} - 1). \quad (3)$$

The linear regression coefficient in Fig. 2 amounts to 0.983. Some of the spread of the points in the figure has to be attributed to the uncertainty in the published polarizability values and to discrepancies between low-energy TCS measurements. Therefore, we believe that Fig. 2 demonstrates the correlation between  $\sigma_z$  values and the square root of polarizability for all molecular targets within the considered range of  $\alpha$ .

We will now demonstrate the validity of the additivity rule for the total-cross-section parameter  $b$ . Note that the additivity assumption on the  $b$  parameter corresponds to additivity of the high-energy asymptotic slopes of TCSs. Our choice implies the validity of the additivity rule for energy regions (the high-energy limit) where the Born approximation is valid.

Starting from our previously measured molecular TCS, we have used the additivity relation

$$b(X_n Y_m) = nb(X) + mb(Y) \quad (4)$$

in the inverse mode, extracting the atomic  $b$  parameters. Different sets of molecules  $X_n Y_m$  can be chosen as a database. For the present work we have obtained the  $b_H$  value for atomic hydrogen as 1/2 of the  $b$  value for  $H_2$ . Note the scarcity of experimental high-energy TCS values for  $H_2$ . For this reason, we used a weighted average of data from Wingerden *et al.* [57] that extend up to 750 eV, from Hoffman *et al.* [58] up to 500 eV, and Zecca, Karwaz, and Brusa [59] up to 2000 eV. Having the  $b_H$  value from  $H_2$ , we have subtracted  $4b_H$  values from the  $b$  value for  $CH_4$  [25], obtaining in this way the  $b$  value for atomic carbon ( $b_C$ ). The value for atomic chlorine ( $b_{Cl}$ ) is obtained from the  $b$  value for the  $CCl_4$  molecule [26]. The atomic  $b$  values derived in this way amount to 0.22, 1.0, and  $3.0 \times 10^{-20} \text{ m}^2$  for H, C, and Cl, respectively. An error of the order of 10% could be attributed to these numbers.

After having obtained  $\sigma_z$  from the molecular polarizability via Eq. (3) and evaluated  $b$  from the additivity rule (4), TCSs for different molecules can be calculated at intermediate and high energies with Eq. (2). In Fig. 3 we present TCSs predicted with the above procedure for  $CH_3Cl$ ,  $CH_2Cl_2$ , and  $CHCl_3$  (together with the fitted values for  $CH_4$  and  $CCl_4$  that served as the database for the atomic  $b$  parameter).

The agreement between our measurements and calculated values is within the experimental error bars in the whole (200–4000)-eV energy range. Deviations from the measured values can be observed below 200 eV for chloromethanes and 50 eV for  $CH_4$ . We have already mentioned that a modified Born-like formula with a low-energy term included [26] gives a better fit to the experimental data than obtained through Eq. (2). It is possible that the use of such a modified formula within the additivity rule procedure outlined above could improve the predicted cross sections below 200 eV. This further step is outside the aim of the present paper. We

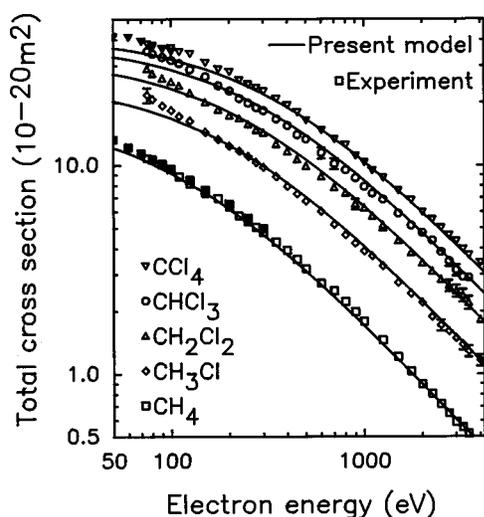


FIG. 3. Comparison between the present semiempirical model [Eqs. (2) and (3) and the additivity rule (4)] and the experimental data for chloromethanes. The symbols have the same meaning as in Fig. 1. The total error bars (one standard deviation of the mean value plus the systematic error) are shown; if not visible the error bars are within the size of the symbols.

stress also that additivity rule cannot be applied at energies where resonant phenomena play a role.

The above procedure and our additivity rule have been applied also to the molecules of the chlorofluoromethanes series  $\text{CF}_4$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ , and  $\text{CFCl}_3$ . Experimental [26,28] TCS values for  $\text{CF}_4$  molecule were used as the database for fluorine atom. The agreement of the calculated TCS values with our measurements [26] is again good; see Fig. 4. Apart from  $\text{CF}_2\text{Cl}_2$ , the agreement remains within the experimental error bars at all energies above 200 eV. Smaller deviations regard only  $\text{CF}_4$  at low energies: Our calculated values for this gas are underestimated by 10% below 400 eV. Adopting for  $\alpha$  a value of  $4.2 \times 10^{-30} \text{ m}^3$  instead of  $3.86 \times 10^{-30} \text{ m}^3$  [52] would bring the  $\text{CF}_4$  data into perfect

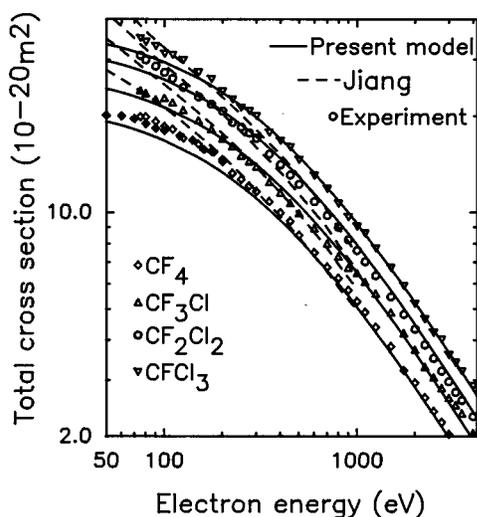


FIG. 4. Comparison between the present semiempirical model [Eqs. (2)–(4)] and the experimental data [26] for chlorofluoromethanes. For  $\text{CF}_4$  the data of Szmytkowski *et al.* [28] are also shown (full rhombuses).

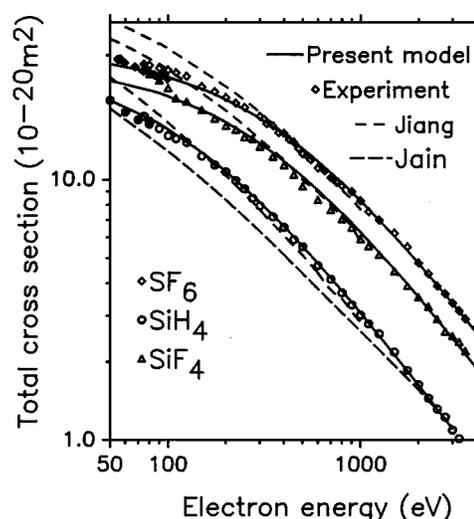


FIG. 5. Comparison between the present semiempirical model, the theory of Jiang *et al.* [30], and the experimental data [26,41] for sulphur and silicon containing molecules.  $\text{SiH}_4$  (full circles), experimental data of Szmytkowski, Mozejko, and Kasperski [65] below 100 eV;  $\text{SF}_6$  (full rhombuses), experimental data of Dababneh *et al.* [66] below 100 eV and (open rhombuses) Zecca *et al.* [41].  $\text{SiF}_4$  [62] (for  $\text{SiH}_4$  the *ab initio* theory of Jain and Baluja [67]) is also shown (long-dashed line).

agreement with experiments [8,26,28]. The  $\text{CF}_2\text{Cl}_2$  calculated values differ from the experiment by a constant (5%) value at all energies above 500 eV. Note that the agreement between experimental and optical-model theoretical values [30] for all gases presented in Fig. 4 is much poorer, with 25% discrepancy at 1000 eV for  $\text{CFCl}_3$  and as much as 50% at 50 eV for  $\text{CF}_4$ .

As a further check of the present formulation of the additivity rule, we have obtained the atomic  $b$  values for Si and S from  $\text{SiH}_4$  and  $\text{H}_2\text{S}$  measurements [39], respectively. Starting from the atomic  $b$  values and using relation (2), we have calculated the  $\text{SiF}_4$  and  $\text{SF}_6$  total cross sections in the (100–4000)-eV energy range; see Fig. 5. Once more, the present model reproduces fairly well the experimental values, giving a much better agreement than the theory of Jiang *et al.* [30]. Values of the high-energy  $b$  parameter for all atoms studied are resumed in Table II.

## V. CONCLUSION

In summary, we have used our formulation of the additivity rule (4) in the inverse mode to calculate atomic  $b$  values

TABLE II. Semiempirical values of atomic cross sections parameter  $b$  (in units of  $10^{-20} \text{ m}^2 \text{ keV}$ ) derived in the present model [Eqs. (2)–(4)].

Atom	$b$
H	0.22
C	1.01
F	1.38
Si	2.57
S	2.94
Cl	3.20

starting from a database of measured molecular cross sections. We have used these values, the  $\sigma_z$  values from polarizability (2), and again the additivity rule in the direct mode to calculate molecular TCSs for as many as eight polyatomic molecules. These calculated cross sections appear to be in

very good agreement with available experiments. This can be held as a proof of the correctness of the present formulation of the additivity rule and the entire procedure. Further developments of the model should deal with polyatomic molecules of different (linear and bent) geometries.

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